New Process for the Production of Better Quality Rapeseed Oil and Meal: II. Detoxification and Dehulling of Rapeseeds — Feasibility Study[1]

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Abstract

Feasibility studies have shown that a white, bland, defatted, thioglucoside-free flour can be prepared from rapeseed. The thioglucosides, the precursors of toxic principles, present in rapeseeds are removed by aqueous extraction. The key operations, boiling of the seed followed by wet-grinding and aqueous extraction, help in the removal of seed coat from the rapeseed. Although aqueous extraction results in the loss of solids, the quality of the end products is good and may offset the loss.

Introduction

Oilseed meal as a rich source of protein is attracting greater attention now than at any other time in the past. Advances in food technology have made it possible to produce simulated meat and dairy products from oilseed meals. Rapeseed ranks fifth in the world production of oilseeds, but the utilization of rapeseed meal as a protein source is limited due to its content of thioglucosides which liberate toxic isothiocyanate and oxazolidinethione upon enzymatic hydrolysis. Destruction of myrosinase, the enzyme responsible for the liberation of the toxic compounds, permits the use of rapeseed meal in the feed rations of livestock and poultry at levels up to 10%. No attempt has yet been made to utilize rapeseed meal as a protein source in human food formulations due to the possibility of recontamination with myrosinase and the presence of black hulls which render it esthetically unattractive.

The following methods for detoxifying rapeseed have been tried: autoclaving (1), steam stripping (2), chemical modification (3) and aqueous extraction (2). Autoclaving or steam-stripping is reported to result in the disappearance of about 90% of the oxazolidinethione (2). However, in studies designed to assess the nutritional value of the protein in rapeseed meal treated in this manner, the same authors observed gradual deterioration in protein quality as the time of heat treatment was extended.

By chemical treatment, the thioglucosides are catalytically decomposed by heating with salts of iron, copper or nickel (3). Of the decomposition products, the toxic, 1-cyano-2-hydroxy-3-butane remains with the meal as it is not steam volatile. It is reported that the water extraction of rapeseed meal to remove the thioglucosides results in an end product which is more toxic than the original material (2).

The objective of the present work was to investigate the technical feasibility of producing a white, bland, defatted rapeseed flour free of thioglucosides and fibrous seed coat. Since the rapeseed thioglucosides are completely soluble in water, the most logical approach to the problem of detoxification would be to seek their elimination by aqueous extraction. Although an extraction step would lead to the loss of some solid matter, it was considered that enhancement of the end product quality would offset the loss. In this paper, the feasibility of eliminating thioglucosides and hulls (seed coats) from rapeseeds for the production of rapeseed flour for human nutrition was studied.

Materials and Methods

Brassica campestris (Echo variety), *Brassica napus* (Tanka variety) and commercial rapeseed meals were used in this study. Enzyme inactivation was performed by the wet-heat treatment method described earlier (4). Extraction data under different conditions were collected as follows. A weighed quantity of meats, crushed seed or commercial meal was extracted with a known quantity of water and the slurry filtered on an 80 mesh screen. The weights of the extract and residue were determined. The total solid content of the extract was determined by drying a known weight of the extract in a Petri dish. The remainder of the extract was freeze dried and used for the analysis of the protein, oil and glucosides. Protein was estimated colorimetrically (5). Oil content of the freeze dried solids was estimated by Soxhlet extraction with petroleum ether. For the estimation of glucosides, samples were shaken with myrosinase solution prepared with phosphate-citrate buffer of pH 7.0. The liberated isothiocyanate and oxazolidinethione were estimated by GLC (6) and spectrophotometrically (7) respectively. The percentage of the different constituents in the extract were calculated from the total solid content value.

Results and Discussion

Typical Four-Stage Extraction

One hundred parts by weight of rapeseed meats were mixed in a planetary mixer with 400 parts of water for 30 min at room temperature. The extract

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TABLE I

Extraction Data on 1:4 See to Water Ratio, Ambient Temperature

Extraction stage	Raw material in extract phase, %	Total thioglucoside in extract, %	Total solid content of extract %	Water hold up on residue %
First	12.48	76.7	3.16	35.0
Second	1.40	9.3	1.07	27.3
Third	0.63	5.9	0.41	25.8
Fourth	0.44	1.7	0.19	27.8
Total	14.95	93.6		

TABLE II

Material Balance Data on 1:4 Seed to Water Ratio, Ambient Temperature

	Per cent of total			
	Thioglucoside	Protein	Oil	Solids
Removed in first extract	49.8	8.12	1.55	8.10
Removed in second extract	26.0	4.3	0.83	4.2
Removed in third extract	11.8	1.5	0.36	1.7
Removed in fourth extract	4.3	0.7	0.18	0.7
Remaining in end product	5.2	85.4	97.00	85.00
	97.1	100.0	99.92	99.70

TABLE III
Effect of Contact Time on Ambient Temperature Extraction, 1:4 Seed to Water Ratio

Agitation time min	Total solids in extract %	Per cent of total in extract		
		Thioglucoside	Oil	Protein
15	2.9	57.4	3.07	9.0
30	3.3	75.3	3.48	10.8
45	3.5	78.4	3.72	12.3
60	3.6	83.5	4.23	14.0

was then separated by filtration on an 80 mesh sieve and the residue re-extracted three times in the same manner. The four extracts and the final residue were weighed and freeze dried separately and estimated for total thioglucoside, protein and oil contents. The extraction data and the analytical data are presented in Tables I and II.

Data in Table I show that 25–35% of the total extract remains with the meats at different stages of extraction. A 10% liquid hold-up was arbitrarily chosen as suitable for this study. It can be calculated that a raw material to water ratio of 1:15 would be necessary to reduce the liquid hold-up to 10% of the total extract. The thioglucoside solubility data presented in Table I show that only about 76% of the thioglucoside has gone into solution during the first stage of extraction. For efficient leaching with the minimum number of extractions, it is essential to have maximum solubility in the first extraction itself. This indicates the necessity to alter the conditions to increase thioglucoside solubility.

Material balance figures given in Table II show a yield of 85% of the raw material with nearly 85% and 97% respectively of total protein and oil.

Similar experiments using aqueous alcohol and aqueous acetone to extract the thioglucosides showed appreciable reduction of extracted matter. However aqueous alcohol or acetone media cannot be used to advantage as it adversely affects thioglucoside solubility.

Effect of Contact Time With Aqueous Media on Thioglucoside Dissolution

One hundred parts by weight rapeseed meats were stirred in a planetary mixer with 400 parts of water at room temperature for 15, 30, 45 and 60 min respectively in different experiments. In each case the extract was separated by filtration on an 80 mesh sieve and analyzed for total solids, thioglucosides, protein and oil content. The values are presented in Table III. The data show that nearly 75% of the total thioglucosides dissolves in the first 30 min period of extraction and that doubling of extraction time does not appreciably increase the amount dissolved. It was observed that, with the increase in extraction time, protein content in the extract increased from 9–14% while the oil content was fairly constant.

TABLE IV
Effect of Temperature on Extraction, 1:4 Seed to Water Ratio

Temperature of extraction (C)	Per cent of total in extract			
	Raw material	Protein	Oil	Thioglucoside
25	12.5	12.5	2.42	76.7
40	14.4	16.6	3.86	85.4
60	15.2	17.5	3.83	88.5
70	16.4	20.0	4.44	82.7
80	16.3	18.1	4.10	91.0

Effect of Temperature on Extraction

One hundred parts by weight of rapeseed meats were extracted with 400 parts of water at 25, 40, 60, 70 and 80 C respectively in different experiments. In each case, the temperature was maintained constant throughout the 30 min extraction period. Coagulation of some dissolved material was observed when extraction was carried out at 80 C. At the end of 30 min the extract was separated by filtration on 80 mesh sieve and analyzed. The values for solids, protein, oil and thioglucosides are presented in Table IV. The amount of protein, oil and thioglucoside in the extract increased with increase in temperature. Extraction at 70 C resulted in an unexplained reduction of glucoside solubility. The slight reduction of protein solubility at 80 C is probably due to partial coagulation.

Extraction of B. napus and B. campestris Seeds and Commercial Meal Samples

In the experiment with rapeseeds the myrosinase was destroyed by soaking the seeds in boiling water for 2 min. The seeds were then passed through a vertical plate grinder with a stream of water to squeeze out the meats from the seed coat (hulls). Sufficient hot water was added to the slurry of rapeseed meats and hulls to adjust the seed-water ratio to 1:15 by weight. The slurry was agitated and maintained at 80 C for 30 min. At the end of the period, it was filtered and the residue re-extracted twice more under the same conditions. The different extracts and the final residue were freeze dried and analyzed for oil, protein and thioglucoside contents.

Commercial rapeseed meal samples (which contain nearly twice the amount of water-soluble matter due to oil removal) were extracted under identical conditions as in the case of rapeseeds except for the lower meal-water ratio of 1:30. The lower meal-water ratio was used to maintain the same water-water soluble matter ratio (in the system) which existed when whole seeds were used for extraction study.

Thioglucoside removal data are presented in Tables V and VI. They show that only in the case of *B. campestris* meal were the thioglucosides dissolved completely at the first stage of extraction. In all cases under study, only 11–16% of the total thioglucosides remained in the seed or meal at the end of the first extraction stage. A minimum of two

TABLE V
Thioglucoside Distribution and Material Balance for Oil, Protein and Solids in 3-Stage, 80 C, Aqueous Extraction of Rapeseeds

Process stage	*B. campestris* seed; percentage of total					*B. napus* seed; percentage of total				
	Thioglucosides		Oil removed	Protein removed	Solids removed	Thioglucosides		Oil removed	Protein removed	Solids removed
	Dissolved	Residual				Dissolved	Residual			
Enzyme destruction	4.2	96.9	....	0.5	1.0	0.5	99.5	....	0.2	0.4
First extraction	92.1	15.8	3.4	10.8	12.5	96.6	15.9	4.9	20.8	20.3
Second extraction	3.5	1.7	1.6	2.6	2.7	2.8	2.1	2.2	4.1	4.1
Third extraction	0.2	0.1	0.7	0.3	0.9	0.1	0.3	0.5	0.9	0.9
Total	100.00		5.7	14.2	17.1	100.00		7.6	26.0	25.7

TABLE VI
Thioglucoside Distribution and Material Balance for Protein and Solids in 3-Stage, 80 C, Aqueous Extraction of Commercial Rapeseed Meals

Process stage	*B. campestris* meal; percentage of total				*B. napus* meal; percentage of total			
	Thioglucoside		Protein removed	Solids removed	Thioglucoside		Protein removed	Solids removed
	Dissolved	Residual			Dissolved	Residual		
First extraction	100.0	10.6	20.6	22.7	96.6	14.6	22.9	25.2
Second extraction	0.0	1.1	4.3	4.5	3.0	1.5	11.9	9.0
Third extraction	0.0	0	2.1	1.8	0.4	0.2	4.6	3.2
Total	100.0		27.0	29.0	100.0		39.4	37.4

extractions were necessary to reduce the thioglucoside residual to 2% or less. A third extraction resulted in almost complete removal of the thioglucosides. Since most of the thioglucosides were dissolved by the end of the second extraction, the possibility of replacing the third extraction with a filter-wash stage is indicated.

The material balance data for oil, protein and total solids are presented in Tables V and VI. The data in Table V show that the yield of the end product from *B. campestris* seed was much higher than that from *B. napus seed.* The increased loss of protein appears to be the main reason for the reduced yield of the finished product from *B. napus* seeds. When commercial rapeseed meals are used, loss of protein through aqueous extraction was nearly 27% and 39% from *B. campestris* and *B. napus* meal respectively (Table VI). The data show that aqueous extraction of either variety of seed results in a smaller loss of protein than from the commercial meals prepared from each seed.

Dehulling (Seed Coat Separation)

One approach to seed coat separation consists in grinding commercial meal and screening it. Glucoside removal by aqueous extraction must, however, precede grinding to prevent increased loss of protein and fine solids in the extract. In the experiment for dehulling commercial meal the finished product obtained after aqueous extraction and drying was powdered and separated into two fractions by screening. The protein content and the percentage distribution of the fractions are presented in Table VII. A fraction with an increased protein content (42–46%) and representing 20–24% of the original commercial meal was prepared by this procedure. The color of the product is dark brown, a quality characteristic which renders the product unsuitable for supplementation or fortification of most foods.

When whole seed is the starting material, seed

TABLE VII
Air Classification of Commercial Rapeseed Meals

	B. campestris meal		*B. napus* meal	
	−80 fraction	+80 fraction	−80 fraction	+80 fraction
Per cent of original raw material[a]	25.3	44.9	20.4	43.3
Per cent protein content[a]	47.2	34.4	49.1	31.2
Appearance	Brown powdery	Dark brown fibrous	Light brown powdery	Dark brown fibrous

[a] Moisture- and oil-free basis.

TABLE VIII
Air Classification of Detoxified Rapeseed Meals

	Meats fraction	Seed coat fraction
Per cent of original raw material[a]	43.9	28.8
Per cent protein content[a]	59.7	33.7
Per cent fiber	10.1	26.5
Appearance	White-powdery	Grey-fibrous

[a] Moisture- and oil-free basis.

TABLE IX
Material Balance for Oil, Protein and Solids in a Semi-Pilot Trial (Average of 10 Experiments Using 80 C Extraction)

	Per cent thioglucoside	Per cent of total		
		Oil	Protein	Solids
Meat fraction	0.0[a]	80.61	62.1	62.2
Seed coat fraction	0.0[a]	14.00	22.3	22.3
Leached out in extraction	100.0	5.39	15.6	17.5
(by difference)	100.0	100.00	100.0	100.0

[a] Not detectable.

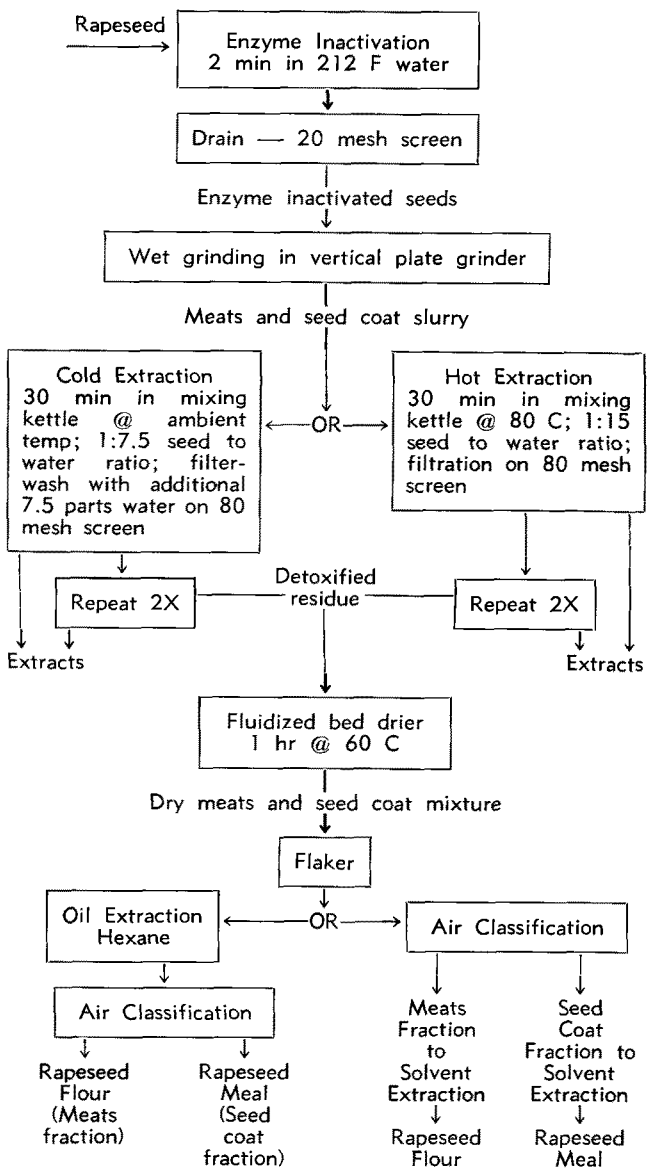

FIG. 1. Flow diagram for preparation of flour and meal from rapeseed.

coat separation can be carried out before or after solvent extraction. As mentioned earlier, grinding of the wet-heat treated seeds in a stream of water results in squeezing out the meats intact from the hulls. The meat-hull mixture after the aqueous extraction and drying, as discussed above, is flaked and air classified into two fractions: a meats fraction (−15 to +20 mesh size) essentially free of seed coat and a hull fraction (−20 to +40 mesh size) containing some powdered meats. The analysis of the products are presented in Table VIII. The data show that nearly 44% of the raw material (moisture- and oil-free basis) can be separated as a white, bland powder containing about 60% protein. The seed coat fraction, also free of thioglucosides, is grey in color and contains about 33% protein (oil-free basis) and could be used as an animal feed.

In recent trials, the meat-hull mixture was solvent extracted, pre-ground and air classified in a commercial unit. Data similar to those in Table VIII were obtained.

Semi-Pilot Plant Trials

Ten semi-pilot plant trials using the hot water extraction procedure for glucoside removal (80 C) were conducted on 10 lb batches of *B. campestris* rapeseed (Fig. 1). The material balance data for oil, protein and solids are presented in Table IX.

Since hot water extraction is expensive and the possibility of a multi-stage cold water extraction was indicated previously (Table I), a cold extraction trial was also carried out (10 lb. batches). To obtain the effect of a 6 stage extraction, a 1:7.5 seed to water ratio was used for each of the 3, 30 min cold water extractions and the remaining 7.5 parts of water sprayed on the filtered residue (Fig. 1).

Current research is directed at the determination of product quality (nutritional, functional and physical) and at optimizing process costs and efficiency.

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